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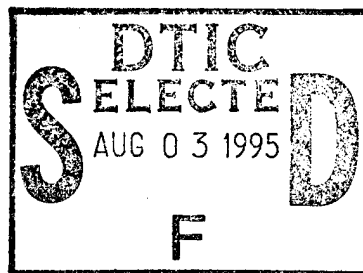


# Thin Films of Novel Ferroelectric Composites

S. Sengupta, L.C. Sengupta, S. Stowell,  
D.P. Vijay, and S.B. Desu

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13. ABSTRACT (Maximum 200 words)  Composites of BSTO combined with other non electrically active oxides have demonstrated adjustable electronic properties which can be tailored for use in various electronic devices. <sup>1</sup> These novel composites of barium strontium titanate (BSTO) and Oxide III compounds have already exhibited promising results in their ceramic form. <sup>2</sup> The additive oxides modify the dielectric constant, tunability (change in the dielectric constant with applied voltage), and dielectric loss of the material. One application has been for use in phased array antennas and insertion has been accomplished into several working antenna systems. <sup>3</sup> To further accommodate the frequencies required by these phased array antennas, thin films of the composites have been fabricated. Preliminary studies have indicated that thin films of such composites exhibit similar behavior as their bulk ceramic counterparts. <sup>4</sup> The purpose of this study is to investigate the properties of the BSTO/Oxide III based compounds in thin film form.				
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## 1. INTRODUCTION

A phased array refers to an antenna configuration composed of a large number of elements that together form a radio beam. The phase of the radio signal at each antenna element is independently controlled. Thus the radio signal can be electronically steered by the active manipulation of the relative phasing of the individual antenna elements. This electronic beam steering concept applies to both the transmitter and the receiver.

Phased array antennas are advantageous in comparison to their mechanical counterparts with respect to their speed, accuracy, and reliability. These complex tracking exercises can be maneuvered better with a phased array antenna system.

Phased array antennas are currently constructed using ferrite phase shifting elements. However, due to the circuit requirements necessary to operate these present day antennas, these are costly, large and heavy. Therefore, the use of such antennas has been limited primarily to military applications which are strategically dependent on such capabilities. In order to make these devices practical for many other commercial and military uses, better materials for antenna elements of the antenna must be developed. Towards this goal, a ceramic Barium Strontium Titanate,  $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ , (BSTO), phase shifter using a planar microstrip construction has been demonstrated.<sup>1</sup> However, to meet the required performance specifications (e.g., maximum phase shifting ability), the BSTO electronic properties must be optimized. As part of this optimization process, various composites of BSTO and non-ferroelectric oxides have been formulated and proven successful.

In order to obtain higher operating frequencies (30 GHz and beyond) and to decrease the voltage requirements, thin film fabrication of the above candidate materials is necessary. This paper outlines the work on the characterization of the thin films of BSTO composites deposited by the pulsed laser deposition (PLD) method. The electronic properties of the films were measured using an HP 4194A impedance analyzer. The results of these measurements will be discussed.

## 2. EXPERIMENTAL

All the thin films in this study were deposited on single crystal sapphire substrates coated with Ruthenium oxide ( $\text{RuO}_2$ ).  $\text{RuO}_2$  was the bottom electrode in the parallel plate capacitor structure created with the BSTO composite thin film as the dielectric and Pt as the top electrode.

The ground plane electrode of Ruthenium oxide ( $\text{RuO}_2$ ) was D.C. sputtered onto the substrates at a substrate temperature of 200 °C and a  $\text{O}_2/\text{Ar}$  ratio of 1:4 with a total pressure of 10 mT. The Ruthenium oxide films were 3000 Å thick. The resistivity of the as-deposited films were on the order of 160  $\mu\text{ohms-cm}$ . They were annealed at 600 °C for 30 minutes to lower the resistivity and were cooled by furnace quenching. The resistivity of the annealed films were measured to be 110  $\mu\text{ohms-cm}$ .

Prior to PLD, the RuO<sub>2</sub> coated sapphire substrates underwent a cleaning cycle which included an ultrasonic cycle of TCE followed by two methanol ultrasonic cycles. The samples were then rinsed with methanol and air dried. The lattice parameters and dielectric constants of the bare sapphire substrates used in this experiment are 4.76 Å and 11 (at 300 K) respectively. The targets chosen for this work were Ba<sub>0.6</sub>Sr<sub>0.4</sub>TiO<sub>3</sub> (BSTO) and BSTO with 1 wt.% of oxide III based compounds. The BSTO composites will hereafter be referred to as Oxide III, Oxide II/Oxide III, Oxide III Compound A, Oxide III Compound B, Oxide III Compound C, and Oxide III Compound D. The PLD of the ferroelectric thin films was accomplished using a Lambda Physik Compex 205 krypton-fluoride excimer laser with a wavelength of 248 nm and a repetition rate of 10 Hz. The substrate was held parallel to the target and their separation distance was maintained at 75 mm. The average pulse energy was 350 mJ with a 20 ns pulse width. The oxygen partial pressure in the chamber was 300 mT and the substrate temperature was 700 °C. The powder pressed ceramic targets were prepared according to a description published previously.<sup>2</sup> A Dektak-200 profilometer was used to measure the films thicknesses. It was measured to be about 3000 Å for all the films. The compositions of the films were confirmed by Glancing Angle X-ray diffraction (GAXRD).

After the deposition of the thin films, the top Pt electrodes were deposited by electron beam evaporation. The thicknesses of the top electrodes were measured to be approximately 2000 Å using a Dektak-200 profilometer.

The dielectric constant ( $\epsilon'$ ) and % tunability were determined for all the thin film/substrate combinations. The % tunability of a material is determined using the following equation:

$$\% \text{ tunability} = \{ \epsilon'(0) - \epsilon'(V_{\text{app}}) \} / \{ \epsilon'(0) \} \quad (1)$$

where  $\epsilon'(0)$  is the real part of the dielectric constant at zero applied voltage and  $\epsilon'(V_{\text{app}})$  is the real part of the dielectric constant at an applied voltage,  $V_{\text{app}}$ . The tunability measurements were taken with an applied electric field which ranged from 0 to +/- 3.3 V/micron ( $\mu\text{m}$ ). The electronic properties were measured at 1 MHz. Capacitance versus voltage (C-V) measurements for the films were taken using an HP4194 impedance/phase gain analyzer.

### 3. RESULTS AND DISCUSSION

#### 3.1 Electronic Measurements

Fig. 1 shows the capacitance versus voltage characteristics at 1 MHz for the BSTO (undoped) film deposited on RuO<sub>2</sub>/sapphire. The dielectric constant at zero bias was calculated to be 1260 and the tunability is 23% at a field of 3 V/ $\mu\text{m}$ . The bulk undoped material has a dielectric constant of 3300 and a tunability of 20% at 0.73 V/ $\mu\text{m}$ .<sup>1</sup> It has been previously shown that the dielectric constant of ferroelectric films are inherently less than the bulk ceramic values due to oxygen defects at the electrode/film interface.<sup>5</sup> Also any porosity and/or leakage current in the films will tend to decrease the dielectric constants obtained.

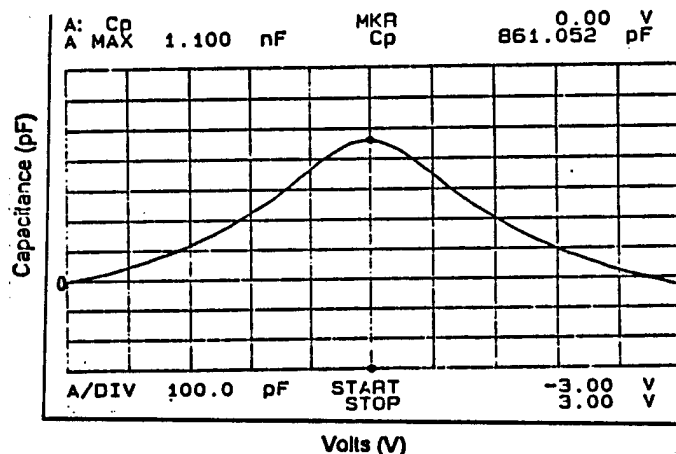


FIGURE 1. Capacitance versus voltage for BSTO (undoped) thin film deposited on  $\text{RuO}_2/\text{Sapphire}$  with Pt top electrode.

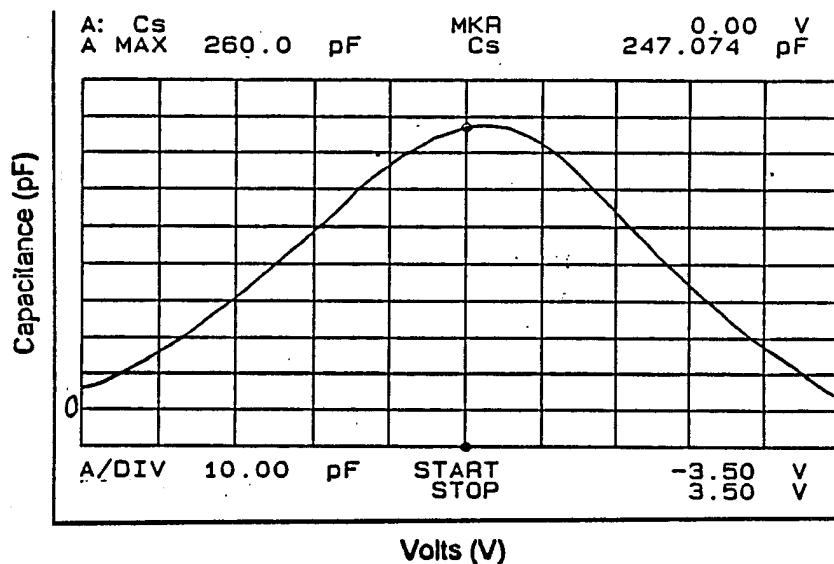


FIGURE 2. Capacitance versus voltage for BSTO/Oxide III thin film deposited on  $\text{RuO}_2/\text{Sapphire}$  with Pt top electrode.

The C-V curve at 1 MHz for the BSTO/Oxide III thin film deposited on RuO<sub>2</sub>/sapphire is shown in Fig. 2. The dielectric constant at zero voltage calculated from this curve is 735. The tunability obtained up to 3 V/μm was 24%. The value for the dielectric constant found in the bulk ceramic target of BSTO/Oxide III was 1276 and a tunability of 16% at 2.32 V/μm.<sup>1</sup>

The C-V curve at 1 MHz for the Oxide II/Oxide III thin film deposited on RuO<sub>2</sub>/sapphire is shown in Fig. 3. The dielectric constant at zero voltage calculated from this curve is 1216. The tunability obtained up to 3 V/μm was 24%. The value for the dielectric constant found in the bulk ceramic target of Oxide II/Oxide III was 2515 and a tunability of 12% at 1.2 V/μm.<sup>1</sup>

Table I summarizes the values of the dielectric constants and tunability of the various BSTO thin films measured at 1 MHz and their ceramic counterparts. The films had a nominal thickness of 3000 Å and the ceramic pellets had an average thickness of 1 mm. As evident from Table I, the dielectric constants of the films are lower than their bulk counterparts. This characteristic has been observed previously in ferroelectric films.<sup>6</sup> The tunabilities of the thin films are self-consistent. However, the tunabilities of Compounds B & C are higher than those of the other bulk compounds. As reported previously,<sup>2</sup> the reason for that has been attributed to higher Curie temperatures. It was also observed that the tunabilities of these thin films did not change substantially with increasing frequency (between 0.25 MHz and 3 MHz).

The thin film of Oxide III Compound A was subjected to an applied bias in the range of 3 V/μm to about 13 V/μm. The effective dielectric constant at 3 V/μm was measured before and after the application of 13 V/μm. This experiment was performed to examine the recovery of the film from higher applied bias. There was about 1% change in the effective capacitance measurement immediately before and after the application of the bias of 13 V/μm.

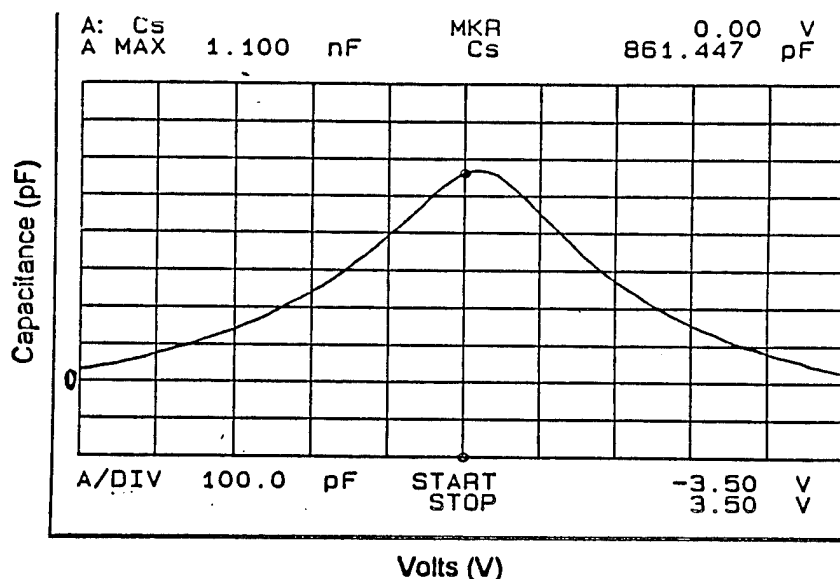


FIGURE 3. Capacitance versus voltage for Oxide II/Oxide III thin film deposited on RuO<sub>2</sub>/Sapphire with Pt top electrode.



TABLE I. Electronic Properties of Thin Film and Bulk Ceramic BSTO/Oxide III Compound Composites.

<u>Material</u>	<u>Applied Field (V/<math>\mu</math>m)</u>		<u><math>\epsilon'</math>(V=0)</u>		<u>%Tunability</u>	
	<u>Film</u>	<u>Bulk</u>	<u>Film</u>	<u>Bulk</u>	<u>Film</u>	<u>Bulk</u>
BSTO	3.0	0.73	1260	3300	23	20
BSTO/ Oxide III	3.0	2.32	735	1276	24	16
BSTO/ Oxide II/Oxide III	3.0	1.2	1216	2515	24	12
BSTO/Oxide III Compound A	3.0	1.7	745	3065	20	19
BSTO/Oxide III Compound B	3.0	2.0	858	3293	14	35
BSTO/Oxide III Compound C	3.0	2.0	1150	2257	12	31

#### 4. CONCLUSION

It has been shown that the thin films exhibit self-consistent tunability to its bulk counterparts even at a lower dielectric constant. It must be emphasized that these tunabilities were achieved with much lower applied voltages than those applied to the bulk.

The mapping of the thickness variation of the films is currently underway in order to establish a true picture of the variation of the dielectric constant over the entire film. It appears from this research that certain additives influence the lowering of the dielectric constant than others even at 1 wt% level. A thorough study of the effect of the additive concentration of oxide III on the lowering of the dielectric constant is underway. The Curie temperature of the thin films will also be investigated to establish the reason for the difference in the tunabilities of Oxide III Compound B and Oxide III Compound C.

Further investigation of such tailoring in the high frequency region through the incorporation of such oxides is also being investigated.

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